Dielectric properties of C₆₀ films in the high-temperature region

J. S. Su and Y. F. Chen

Department of Physics, National Taiwan University, Taipei, Taiwan, Republic of China

K. C. Chiu

Department of Physics, Chung-Yuan Christian University, Chung-Li, Taiwan, Republic of China

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Capacitance and dissipation factor measurements of the dielectric properties on C₆₀ thin films are performed at a temperature between 275 and 470 K. A Debye-like relaxation in the dielectric response has been observed, and the relaxation rate is thermally activated with an energy of about 467 meV which is different from the value 277 meV obtained at a temperature below 260 K. Remarkably, both the capacitance and dissipation factor curves as a function of temperature have a pronounced feature at 435 K. It confirms the fact that above 400 K a phase transition does occur in the C₆₀ crystal except for that detected around 260 K. We interpreted the phase transition at 435 K in terms of the disappearance of one of the spherical harmonics Y_l^m that describe the orientational density distribution of the C₆₀ molecules. © 1999 American Institute of Physics.
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The recent development¹ of an efficient synthesis of the C₆₀ crystals has attracted intense researches and led to a number of exciting discoveries, including the observation of superconductivity² in alkali-metal-doped C₆₀, persistent photoconductivity,³ and the orientational order-disorder phase transition.⁴ It is now well known that at 260 K an order-disorder phase transition occurs in the C₆₀ crystal. In the low temperature phase ($T < 260$ K), the C₆₀ molecules jump between two different orientational states and undergo a thermally activated process with an activation energy of about 277 meV. Above the phase transition temperature, the C₆₀ molecules rotate isotropically and freely. But in the single C₆₀ crystals Fortune *et al.*⁵ obtained a peak of the heat capacity at 425 K and Aral *et al.*⁶ observed a broad hump around 450 K by detecting the C₆₀ electrical resistivity. Hamanaka *et al.*⁷ detected a sharp Raman band above 400 K. Recently Yan and Wang⁸ reported that the internal friction of the C₆₀ crystal has a drop at 426 K. All those results show that a phase transition might happen and a partial orientational order might remain in the C₆₀ solid above 400 K. But the definite answer still needs more concrete evidence probed by other measurements. The dielectric properties of a solid are very sensitive to the local electrical field distribution within the samples, and thus provide an excellent opportunity to probe the phase transition and defect properties of the C₆₀ solid. However, the dielectric properties of the C₆₀ crystal have only been reported by several letters,^{9–11} and the results are rather controversial. For example, Alers *et al.*⁹ observed a Debye-like relaxation in their dielectric studies, but they did not detect the glass transition. Yan and Wang¹¹ did not observe the Debye-like relaxation, but a weak signature of the glass transition was detected at 85 K. In addition, all the experiments were performed in a low temperature range ($T < 300$ K). Obviously, more work has to be done on the dielectric studies of the C₆₀ solids. In this letter, we present capacitance and dissipation factor measurements of the C₆₀ thin films from 275 to 470 K. We have detected a Debye-like relaxation in the dielectric response, which

shows the existence of electric dipole moments in the C₆₀ films. We showed that the relaxation rate is thermally activated with an energy of 467 meV, which is quite different from that obtained in the temperature below 260 K. Furthermore, the capacitance and dissipation curves confirm the structural phase transition at 435 K. We attributed this phase transition to the disappearance of one of the spherical harmonics Y_l^m that describe the orientational density distribution of the C₆₀ molecules. Our result indicates that the partially orientational order do exist above 260 K.

Thin films were grown by sublimation of the C₆₀ powders onto Au coated sapphire substrates held at 300 °C. The starting material is commercially available 99.95% C₆₀ powders. The films were coated with 1000 Å Au top contacts. From the measurements of scanning electron microscopy, the C₆₀ films were microcrystalline with an average grain size around 10 μm.¹² The capacitance C and dissipation factor D measurements were performed using a HP 4284A LCR meter in a He dewar with a Si diode as the temperature thermometer. The capacitance and the dissipation factor can be measured over the frequency range from 20 Hz to 1 MHz and the temperature range from 4.2 to 500 K. Sensitivity to relative changes in capacitance was better than 10⁻⁵. The complex dielectric permittivity $\epsilon = \epsilon' + i\epsilon''$ can be transformed from the capacitance C and the dissipation factor D as follows:¹³

$$\epsilon' = Cd/A\epsilon_0 \quad (1)$$

$$\epsilon''/\epsilon' = D = \tan \delta, \quad (2)$$

where d is the width of the metal contacts, A is the contact area, and ϵ_0 is the permittivity of free space. The dissipation factor D is defined as the dielectric loss tangent $\tan \delta$. Further details on sample preparation and film characteristics are given elsewhere.^{12,14}

Figure 1 shows the dissipation factors versus the temperature measured with three selected frequencies. The D curves indicate distinct behaviors in different temperature re-

FIG. 1. Dissipation factor D vs temperature T with three selected test frequencies (5, 10, and 25 kHz) for the C_{60} film. A peak without a shift appears at 435 K.

gions. At $T \sim 435$ K, a peak is clearly detected and does not shift with changing frequencies, which is quite different from that due to the Debye-like relaxation. The temperature of this peak is similar to that of the phase transition observed by other techniques measured in a high temperature regime.⁵⁻⁷ The noticeable difference is that the dissipation spectra exhibit a much more pronounced feature. Here, we can see that the dielectric response is a very powerful tool to probe the phase transition as compared with other techniques. At the temperature range from 275 to 400 K, as shown in Fig. 2, we observed a broad hump between 300 and 360 K. As the test frequency increases, the peak around 300 K moves to a higher temperature, which suggests a temperature-dependent relaxation time. It indicates a Debye-like relaxation has been detected in the dielectric response spectra. In an effort to see the temperature dependence of the peak position, the logarithm of the test frequency $\ln f$ versus the reciprocal of the peak temperature at the corresponding frequency is plotted in Fig. 3. We can see that $\ln f$ and T obey the equation

$$f = f_0 \exp(-E/k_B T), \quad (3)$$

where f_0 is a constant, k_B is the Boltzmann constant, and E is the activation energy. This behavior indicates that the relaxation process is thermally activated. From the slope the obtained activation energy is about 467 meV, and the value of f_0 is 2.63×10^{11} Hz. The activation energy 467 meV is different from that 277 meV of the Debye relaxation measured at a temperature below 260 K.⁹ The observation of the Debye-like relaxation that requires the existence of electric dipole moments in the C_{60} solid seems quite surprising for a system that has a centrosymmetric crystal. Nevertheless, the electron localized states are always induced by defects. We believe that the defects responsible for the required distribution of the barrier energies for the carrier hopping break the local inversion symmetry and allows the dipole moment to exist. So, the electric dipoles induced by the orientational defects both make the capacitance increase slowly in Fig. 4 and also show the dielectric relaxation process in Fig. 2. It is also possible that the extrinsic dipoles of material impurities are responsible for the relaxation. But judging from the purity of our sample this seems unlikely. From our result, we

FIG. 2. Dissipation factor D curves measured at different frequencies have been amplified between 275 and 400 K. The arrows indicate the peak position which shift with the changing test frequency.

thus obtain that the defects responsible for the carrier hopping below 260 K are different from those above 260 K.

Figure 4 shows the capacitance versus the temperature measured at 5 kHz. In the higher temperature range, the capacitance curve rises rapidly from 410 to about 430 K and has an obvious drop around 435 K, which is consistent with the phase transition temperature measured by the dissipation factor. Below 410 K, through the expanded view at $275 \text{ K} < T < 400 \text{ K}$ the capacitance has a weak hump around 350 K as shown in Fig. 4, which is similar to the structure observed in the dissipation factor measurements. We can also see that

FIG. 3. The natural logarithm of the test frequency $\ln f$ vs $1000/T$. The line is fitted to an Arrhenius temperature dependence given by Eq. (3).

FIG. 4. Capacitance as a function of temperature measured at 5 kHz. Inset: Expanded view of capacitance at $275\text{ K} < T < 400\text{ K}$.

the capacitance above 435 K is higher than that below 435 K.

Let us now provide a possible mechanism to interpret all the earlier results. Recently, both the experimental and theoretical works indicate that the orientational intermolecular correlation do exist above 260 K. For example, some x-ray experiments did observe evidence of complex short-range orientational correlation above 260 K.^{15–17} In the theoretical aspect, Michel, Copley, and Neumann¹⁸ showed that the molecular orientational density distribution is composed of spherical harmonics Y_ℓ^m . Molecular symmetry implies that nonzero terms are those with $\ell=0,6,10,\dots$. In the orientationally ordered phase when the C_{60} molecules rotate freely and isotropically, the corresponding spherical harmonics is Y_0^m . For the orientationally ordered phase, the spherical harmonics has a nonzero ℓ , and the intermolecular orientational correlation exists. Considering the repulsive interaction, Michel, Copley, and Neumann¹⁸ found that the order-disorder phase transition at 260 K can be attributed to the appearance of Y_{10}^m below 260 K. According to their theory, different spherical harmonics will disappear at different temperatures. Therefore, we anticipate that except at 260 K, the orientational order-disorder phase transitions may occur at other critical temperatures which correspond to the disappearance of different spherical harmonics, such as 435 K observed here. Based on this argument, our results obtained earlier can be easily explained. Because different spherical harmonics can create different orientational defects, thus, the activation energy of the carrier hopping among these defects should have different values for the temperatures above and below 260 K. This behavior is just what has been observed.

Furthermore, the disappearance of one of the spherical harmonics will generate additional defects, which enhances the hopping probability, thus, the fact that the capacitance above 435 K is higher than that below 435 K is expected. Therefore, we can see that if we attribute the phase transition at 435 K to the disappearance of one of spherical harmonics, our results can be explained consistently.

In summary, we present the dielectric study of the C_{60} films using the capacitance and dissipation factor measurements at a temperature between 275 and 470 K. A Debye-like relaxation has been observed in our measurements below 400 K. We found that the relaxation rate is thermally activated with an energy different from that of the Debye-like relaxation below 260 K. Both the capacitance and dissipation factor curves clearly show a structural phase transition at 435 K. Based on the previously developed theory, we attributed this phase transition in terms of the disappearance of one of the spherical harmonics that describe the orientational density distribution of the C_{60} molecules.

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